

SEMI-ANNUAL PROGRESS REPORT

NATIONAL AERONAUTICS AND  
SPACE ADMINISTRATION

GRANT NO.  
NsG-100-60

Rensselaer Polytechnic Institute  
Troy, New York

September 1967

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Semi-Annual Progress Report  
National Aeronautics and Space Administration Grant NsG-100-60  
March 1, 1967 to August 31, 1967

INTRODUCTION

The Interdisciplinary Materials Research Program at Rensselaer Polytechnic Institute has grown both in size and depth since the program was inaugurated in 1960. The interdisciplinary concept at Rensselaer has spread to other areas of the campus to the degree that the generally accepted concept of academic departments in Rensselaer's Engineering School has given way to a newly announced reorganization of the school, which is more interdisciplinary in nature.

When the NASA supported Interdisciplinary Materials Research Program was initiated at Rensselaer, it involved ten professors and seventeen graduate students from five academic departments. The research laboratories were located in an old, crowded dormitory that had been renovated to provide the necessary laboratory space. The ensuing seven years, however, have seen the program develop so that currently twenty professors and about sixty students are conducting basic research in materials under the NASA supported program in a 51,000 square foot building which was erected in 1965 with funds provided by a NASA facilities grant. As one example that the interdisciplinary concept is truly working, a recent review of the work going on at the Center's electron optics facility revealed that twenty-one different research programs involving nine separate academic departments were using the facility's equipment and expertise. In addition, several other research programs have consulted its electron microscopy group for intermittent assistance.

NASA support has enabled Rensselaer to acquire the sophisticated equipment so necessary if a university is to be on the forefront of basic research. A new major facility being developed in the Center is a mass spectrometer laboratory acquired with the aid of NASA and NSF funds. A unique feature of this facility will be the spectrometer's Knudsen cell which allows studies of solid materials in the vaporized state at high temperature. The basic equipment will be used generally for the characterization of new organic compounds with particular emphasis on polymer structure.

The Interdisciplinary Materials Research Program still derives its guidance from the Faculty Committee on Interdisciplinary Materials Research. The Committee members meet periodically to review the on-going programs, to consider new programs, and to make overall policy decisions concerning the long range plans. NASA has provided close technical liaison between their organization and the Committee. The periodic visits by NASA technical representatives have provided inspiration to Rensselaer's program as well as assurance that the basic research being conducted is in consonance with NASA's goals.

As of 1 April 1967, NASA support of Rensselaer's Interdisciplinary Materials Research Program has provided funds to partially support the education of eighty graduate students. Of this number, thirty-five received master degrees and forty-five received doctoral degrees. It is interesting to note that almost half of

these degrees were awarded during the two years immediately preceeding April 1, 1967 reflecting the increasing rate of degree output. At the time of the April survey, forty-seven graduates were working for industry, six for the government, and the remainder were employed either by universities or research institutes or were continuing their education.

Industry has profited in other ways from the spin-off of Rensselaer's NASA supported materials research activities. During the summer of 1967, Rensselaer presented a course entitled, Metallurgical Applications of Electron Microscopy which was attended by twenty-four participants, sixteen of whom represented industrial organizations. This course could not have been held without Rensselaer's modern electron optics facilities available in the Materials Research Center. Dr. G.S. Ansell, Robert W. Hunt Professor of Metallurgical Engineering and Dr. Gary Judd, Assistant Professor of Metallurgical Engineering, conducted this course. An additional example of spin-off for industry is the Glass in Electronics series under the direction of Dr. J.D. Mackenzie, New York State Science and Technology Professor of Ceramics and Glass. This significant area of research was developed with major support under this contract. The lecture series was funded by the New York State Science and Technology Foundation. One hundred and eleven industrial scientists participated in this series which had a total attendance of one hundred and seventy-eight.

It will be noted that this thirteenth Semi-Annual report follows a different format from that of previous reports. The Interdisciplinary Materials Research Program has four discrete areas of emphasis; Inorganic Non-Metallic Materials, Metallic Solids, Polymers, and Solid State Physics. A separate section of the report deals with each of these areas. Each section contains a brief introduction which gives the general nature and scientific impact of the research being conducted. This introduction is followed by more detailed technical reports for each specific project.

INORGANIC NON-METALLIC MATERIALS

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The inorganic non-metallics Interdisciplinary Materials Research Program at Rensselaer presently includes activities on both ceramics and semiconductors. Ceramics and semiconductors include an extremely large number and large variety of materials. The small program at Rensselaer is obviously selective. It is also concerned mainly with the "newer" or "fore-front" aspects of these materials. All these involve the preparation, properties and structures of materials which are stable at high temperatures and which have interesting electrical and mechanical properties. The total effort is undertaken by three professors and ten graduate students.

High temperature, high strength materials such as the metal nitrides, carbides and borides are of particular importance in aerospace applications. They are relatively difficult to prepare by reacting the solid constituents. The powdered solids so formed are also difficult to form into intricate shapes by conventional techniques. These materials, however, can be easily prepared by reactions in the vapor phase and subsequent condensation onto substrates of a desired shape. This important aspect of the preparation of high temperature materials is one of the areas being studied.

Glasses have always been considered as electrical insulators. Recently, it has been discovered that many glasses can be made which have very interesting semiconducting properties. These are either based on transition metal oxides such as iron oxide or the chalcogenides such as selenium and sulphur. The two types and their mixtures form a new group of glassy semiconductors which are being studied.

Since some of these glasses are difficult to prepare by conventional methods, new techniques have been developed for their formation. Such techniques are also being exploited for the preparation of new non-crystalline materials. Some of the less common crystalline semiconducting solids such as manganese selenide which are important in communication devices are being investigated. These comprehensive studies include thermodynamics and kinetics of gas phase reactions and measurements of electrical properties. A description of the three programs is given below.

NCN-CRYSTALLINE SOLIDS

Senior Investigator:	J.D. Mackenzie, Ph.D. Professor of Materials Science
Research Staff:	W. Frey, B.S. Graduate Assistant J. Miller, B.S. Graduate Assistant J. Neely, B.S. Graduate Assistant J. Lang, M.S. Graduate Assistant

The objectives of this work is to correlate structures and properties of glasses and uncommon non-crystalline solids. During this period, research has been carried out on:

- a) The preparation of crystalline and non-crystalline silicon nitrides and a study of their optical properties. Silicon nitride is an important insulator for electronic devices.
- b) The factors which influence hardness of simple glasses such as silica. It is perhaps surprising that no definition of hardness of glass exists. This work has resulted in a general understanding of "what is hardness" and a definition.
- c) The preparation of a new type of glass called oxychalcogenides which is obtained by co-melting a selenide such as  $\text{As}_2\text{Se}_3$  and an oxide such as  $\text{CuO}$ . These form a new family of semiconducting glasses with interesting electrical properties.
- d) The preparation of non-crystalline transition metal oxides such as  $\text{NiO}$  and  $\text{FeO}$  and a study of their optical and electrical properties. The objective is to compare these properties for crystalline and non-crystalline solids.

All these projects will be continued in the next period.

During the period, J.D. Mackenzie was invited by the Soviet Academy of Sciences to lecture in Leningrad in May. Two lectures were given on the above research.

PYROLYTIC MATERIALS

Senior Investigator: R.J. Diefendorf, Ph.D.  
Associate Professor of Metallurgical  
Engineering

Research Staff: R. Mehalso, M.S.  
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F. Buschmann, B.S.  
Graduate Assistant

Epitaxial growth of chemically vapor deposited materials has received sustained interest by the semiconductor industry. Less research has been performed at higher supersaturations where two dimensional non-coherent nucleation occurs. At present, we are investigating the general relationship between super-saturation, and substrate temperature for a wide range of refractory materials such as boron nitride, silicon nitride, and titanium diboride. Particular emphasis has been placed on conditions which yield extremely high nucleation rates and produce strong microcrystalline or amorphous deposits.

An in depth study has also been started on the nucleation and growth of graphite deposits and the relation of structure and properties. This study on graphite is more complex since gas phase nucleation also occurs. We are now trying to separate the effects of gas phase nucleation and growth from surface phenomena.

In a former area of research which was funded for part of the time by NASA, a paper on the "Effect of Impurities on the Deposition of Pyrolytic Graphite" was presented at the Eight Biennial Conference on Carbon by B.L. Butler and R.J. Diefendorf. The paper will be submitted to the journal "Carbon."

HIGH TEMPERATURE AND SOLID STATE CHEMISTRY

Senior Investigator: H. Wiedemeier, Ph.D.  
Associate Professor of Chemistry

## Research Staff:

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Graduate Assistant  
A. Khan, B.S.  
Graduate Assistant  
A.G. Sigai, B.S.  
Graduate Assistant  
H. Sadeek, B.S.  
Graduate Assistant

The objectives of this work are to determine the thermodynamic and kinetic properties of solid phase - gas phase reactions of transition metal chalcogenides, and secondly, to study the electrical and optical properties of some of these materials.

The thermodynamic studies lead to values for the energies required to vaporize or decompose materials under rarefied atmospheres as they exist in space and at high temperatures. The kinetic studies reveal the actual mechanism of such processes. Both results are immediately related to the stability of materials.

The investigation of electrical and optical properties is of great interest for such important applications as communication devices.

Both aspects of our work require well defined materials of highest purity and for some parts in form of single crystals.

Single crystalline manganese sulfide, selenide, and telluride, cadmium sulfide, selenide, and telluride, and single crystals of some ternary mixtures have been grown by chemical transport techniques. This method is based on the formation of an intermediate gaseous molecule and crystal growth from the vapor phase. The application of high purity starting materials in a continuous close-system process leads to large sized crystals of high purity. We have grown MnS crystals in form of ultra-thin platelets of up to  $1 \text{ cm}^2$  in area, MnSe tetrahedra and octahedra of several mm edge length, and CdS hexagonal columns of about 1 cm in size. The crystals are nearly perfect and show in many cases mirror-like faces.

The thermodynamic studies on MnSe under equilibrium conditions (low pressure,



high temperature) have been completed and yielded enthalpies and entropies of vaporization. In connection with these studies, a theoretical treatment for the evaluation of data for partially dissociated species as they occur mainly in this system has been developed. The results of this work have been submitted for publication.

Kinetic studies on this system to reveal the actual mechanism of vaporization are in progress.

The degree of solid solution in the MnS-CdS system has been investigated over a temperature from 600° to 1000°C and over the entire range of composition. Mixtures of various mole ratios were pressed to pellets, annealed at the corresponding temperature, quenched, and the phases present were determined by x-ray diffraction techniques.

The two-phase region extends from about 50 mole percent MnS to 90 percent at an intermediate temperature. Studies are in progress to determine the free energy of various composition in the single phase regions in order to establish free energy phase diagrams.

Electrical measurements on pressed polycrystalline samples are used for orientative purposes. Such problems as ohmic contact, grain boundary resistance, and surface conductivity restrict reliable and precise measurements of electrical properties to the use of single crystals. Experiments are under way to grow mixed single crystals for these studies. Preliminary results indicate that mixed single crystals can be obtained by vapor transport techniques.

These investigations are extended to other systems of manganese chalcogenides and II-VI compounds. Emphasis is placed here on the solid state studies with a special interest in developing techniques for the synthesis of mixed single crystals of pre-selected properties.

## METALLIC SOLIDS

## METALLIC SOLIDS

Four of the studies under the Interdisciplinary Materials Research Program are concerned with metallic solids. The unique electronic structure of metallic solids gives rise to the characteristic properties of metals and alloys. Because of the type of interatomic binding forces found in metallic solids, they form crystalline structure which combine good strength properties with ductility. This phenomenon is in contrast to other crystalline solids which may have high strength, but are generally brittle. The electronic structure of metallic solids causes high electrical and thermal conductivity and determines their chemical properties.

The properties of metallic solids - in particular the details of their mechanical and electrical behavior - cannot be understood on the basis of the electronic structure of these materials alone. Two other types of structure must also be considered. One of these is the defect structure of metallic solids, i.e. the number, distribution, and arrangement of vacancies, dislocations, stacking faults and other defects in the crystal lattice. The other type, generally termed the "microstructure" of metals and alloys, is concerned with the examination of metallic solids under the optical or electron microscope. These observations include the size of the individual crystals, called grains, and the arrangement and distribution of the different types of crystalline aggregates, called micro-constituents.

All of the studies being conducted under the metallic solids program may be viewed under the aspect of investigating structures and their effect upon the properties of metallic solids. Of particular interest to the investigators are, on the one hand, the mechanical properties of metals and alloys and, on the other hand, their chemical properties, in particular their corrosion resistance. One project combines mechanical and chemical properties, since stress corrosion is concerned with the interrelationship between stress and chemical attack.

The effects of dislocations, which are defects in the crystalline structure upon the formation of a fine dispersion of a second constituent in a matrix metal,

are being investigated. Alloys of this nature, the so-called dispersion strengthened alloys, are of great practical importance because of their superior mechanical properties at elevated temperature. The aim of this study is to provide a better understanding of the mechanisms by which such dispersions are formed. Their formation is closely dependent upon the defect structure of the matrix metal, and some of the most recent work has indicated that the physical properties also depend on the electronic structure of the alloys being investigated. The relation of properties to all three types of structure, is, therefore, being studied.

A second project involving dispersion strengthened alloys, principally powder metallurgy, is concerned with methods of producing dispersion strengthened alloys by powder metallurgical techniques on the one hand, and by techniques based upon fusion metallurgy, viz. internal oxidation, on the other hand. In general, one would expect that the properties of alloys would depend solely upon their structure, electronic, defect or metallographic. The validity of the concept is being tested by correlating structure and properties of dispersion strengthened alloys produced by different methods.

Another investigation in progress is concerned with the chemical properties of alloys, in particular their corrosion behavior. The method of electrode kinetics which give a more basic understanding of corrosion behavior than the usual empirical corrosion studies is being used. The aim of this work is to relate the corrosion behavior to the composition of the alloys. Since variations in composition are related to the electronic structure of an alloy, this work might be termed an investigation of the relation of electronic structure to chemical properties. The present approach must necessarily be empirical, since our understanding of the direct relationship between composition of alloys and their electronic structure is still rudimentary.

A study on stress corrosion is also concerned with correlations between mechanical properties, i.e. crack formation, and composition. The situation is even

more complex than in the case of straight corrosion studies, since not only the composition of the alloy, but also that of the environment determines crack formation under stress. Stress corrosion is of great practical importance but is not yet well understood. It has been found that stress corrosion is closely allied with the formation of oxide films on the alloy. The conditions under which these films are formed are being investigated.

DISPERSION-STRENGTHENED MATERIALS

Senior Investigator:	F.V. Lenel, Ph.D. Professor of Metallurgical Engineering
Research Staff:	Robert Wyckoff, B.Mat.Eng. Graduate Assistant Mohamed Y. Nazmy, B.S. Graduate Assistant Kai Chia Wang, B.S. Research Fellow

The effort to produce dispersion-strengthened alloys by several different methods is being continued. The aim of this study is to compare the mechanical properties of such alloys. An attempt will be made to produce alloys with as nearly as possible the same structure in order to determine whether they have the same properties.

Alloys consisting of a dispersion of germanium oxide in silver were found to be unstable at high temperatures. Alloys produced by internal oxidation of silver-germanium solid solution alloys exhibited rapid coarsening. They are therefore not suitable. Alloys consisting of a dispersion of gallium oxide in silver have been produced by two methods:

- 1) Internal oxidation of silver-gallium solid solution alloys.
- 2) Co-precipitation of silver and gallium hydroxides from an aqueous solution with sodium hydroxide, decomposing the mixture of hydroxides into a mixture of elemental silver and gallium oxide and consolidating the mixture into an alloy.

The alloys are considerably stronger than pure silver and appear to be reasonably stable.

The investigation of creep in pure aluminum is being continued. In addition to obtaining creep data, the structure of the alloys is determined by electron microscopy.

A STUDY OF THE INTERACTION OF DISLOCATIONS WITH DISCRETE SECOND-PHASE PARTICLES  
IN DISPERSION-STRENGTHENED ALLOYS

Senior Investigator:	G.S. Ansell, Ph.D. Professor of Metallurgical Engineering
Research Staff:	G. Judd, B.Met.E., Ph.D. Research Associate (received Ph.D. 6/67, now Assistant Professor) E. Breinan, B.Met.E., Ph.D. Research Fellow (received Ph.D. 6/67) D. Passoja, B.S. Graduate Assistant R. Bradt, B.S. Research Fellow R. Messler, B.Met.C. Research Fellow P. Renavikar, B.S., M.S. Graduate Assistant C. Grove, B.Met.E. Research Fellow A. Cohen, B.Met.E. Graduate Assistant

The primary objective of this program has been to delineate the effects associated with the presence of a distributed second-phase in a crystalline matrix by both theoretical considerations and experimental observations. Additionally, the program of research has expanded in scope to include other aspects of the role of the defect and microstructure of crystalline solids upon both physical and mechanical properties.

During this period, research efforts have centered principally upon experimental observations utilizing both replication and thin film transmission electron microscopy techniques. The specific areas investigated include:

A. Precipitation Kinetics

In studies of the formation of precipitate phases from solid solution, interest has generally centered upon the interaction of the solute elements with the quench and solute induced defect structure in conjunction with models of heterogeneous nucleation. In our studies of the Al-Ag system, several observations apparently consistent with this approach were noted. It has since become evident

that rather than simply falling into this classical pattern of defect structure-solute interaction, one could more rationally treat the precipitate formation on a much more fundamental basis; i.e., using band theory arguments. A series of Al-Ag-X alloys have been made in which the electronic structure of the alloy has been changed both by choice and amount of the X element, and by the vacancy concentration in the alloys. The aging kinetics of these alloys has been studied by means of transmission electron microscopy and these observations then correlated with theoretical computations using rigid band models. It appears that it is possible to predict on the basis of the rigid band models the sequence of formation of defect structure and precipitate phases and their interrelationships in these alloys and these models should be generally applicable to other alloy systems. The preliminary results of this approach was presented as an invited paper at the 1967 annual meeting of the AIME in Los Angeles, and papers covering this work are currently being prepared for publication.

#### B. Martensite Transformation

The kinetics of the martensite transformation in the Fe-C system have proved elusive. As a result of recent work in this laboratory, it is felt that this transformation may be controlled by the shear strength of austenite. For this reason an investigation of the kinetics of the martensite transformation as a function of austenite strength has been undertaken.

Several approaches are being used in this study. In the first, the effect of solute elements of varying diffusivity in austenite upon the nature of athermal stabilization during rapid quenching is being studied. We have established that such rapid quenching increases dramatically, as much as 200°F, the  $M_s$  temperature of 52100 steel. We now wish to establish the role of the solute elements in steel upon this aspect of the transformation kinetics. This program has centered about



determining the effect of quench rate upon the  $M_s$  temperature of Fe-C-X alloys in which the nominal  $M_s$  temperature of these alloys are identical and the effect of the X element on carbon diffusivity is quite variable. This program is now in progress. The results to date indicate that the quench rate effect of the  $M_s$  temperature is directly related to the rate of carbon diffusivity in the austenite as predicted by the strengthening model previously proposed.

The second approach has been to determine the effect of the shear strength of austenite upon the transformation. An apparatus was constructed so that specimens could be austenitized and then quenched and held just above the  $M_s$  temperature, deformed in tension so as to work-harden the austenite, and then quenched to martensite in a magnetic field. This provides a quantitative measure of the relationship between the  $M_s$  temperature and the flow stress of austenite. It was found that the  $M_s$  temperature was, as predicted, directly a function of the shear strength of the austenite. A quantitative model was then developed linking the transformation temperature to the energy required for the shear transformation. This work is now completed, forming the doctoral dissertation of E.M. Breinan. A paper covering this study is currently being prepared for publication.

The third approach has been to relate the entire transformation kinetics to the flow stress characteristics of the austenite. In order to accomplish this, a series of oxide dispersion-strengthened Fe-C-Mn alloys are being prepared in which the oxide content of the alloy series is varied from 0 to 15 vol. % in order to vary the shear characteristics, but not the free energy of the alloys. These alloys are being prepared by powder metallurgy techniques. Several have been fabricated at this time, and the remainder should be completed shortly. The intention is to determine the martensite transformation kinetics of this alloy series, and to relate these to their shear characteristics. This program is currently in progress.

### C. Thin Film Microprobe

A recent development in the instrumentation useful to workers in the field of structure-property relationships in crystalline solids has been the combination thin-film x-ray fluorescent microprobe unit and electron microscope. This instrument provides the means for not only resolving the detailed micro and defect structures of thin foil specimens with the inherent resolution of the electron microscope, but also permits the determination of the composition of the specimen on a microscale. There are, however, experimental limitations which have been inherent to this type of thin foil probe in providing quantitative rather than qualitative data. These are principally: 1) The specimen area is sampled non-uniformly; i.e., the area of view and hence the portion of the specimen being analyzed is probed by an electron beam whose intensity varies across the field of view. As a result, variations in composition analysis result from changes in specimen location within the field of view, and 2) Most of the electron beam is transmitted through the specimen and does not interact with the specimen to produce the x-ray fluorescent output. (This is contrasted with bulk probe work where the entire electron beam interacts with the specimen). As a result primarily of these factors, the use of such instrumentation has not been as valuable as would otherwise be the case.

During this program period, studies were initiated to develop experimental techniques to obtain data which would permit the quantitative useage of this potentially very valuable instrumentation in our experimental program.

As a result of these studies, techniques have been developed which permit the determination of: 1) the energy distribution within the electron beam, 2) x-ray fluorescent output as a function of specimen composition and thickness, and 3) the application of these methods to permit quantitative chemical analysis of areas of foil specimens which are much smaller than the beam diameter; e.g., it is now possible to determine the composition of two different submicron precipitate phases

in a duplex precipitation hardened alloy. This work is now completed, forming the doctoral dissertation of G. Judd, and papers covering this work are being prepared for publication. It is now planned to utilize these techniques in studies of defect structure induced microsegregation in alloys.

#### D. Domain Boundaries in Ferroelectrics

The nature of domain boundary interactions in ferroelectric barium titanate is being investigated by means of transmission electron microscopy. Although this study is primarily directed towards understanding the peculiar dielectric aging phenomenon that occurs following the ferroelectric transition, the domain boundary behavior approach is expected to also strengthen our understanding of domain processes in ferroelectrics. The transmission electron microscopy studies are being supplemented with structural studies by means of optical polarized light microscopy and detailed electrical measurements of the kinetics of the aging process.

This program is currently in progress and should be completed within the next program period.

#### STRESS CORROSION CRACKING OF COPPER-BASE ALLOYS

Senior Investigator:	N.S. Stoloff, Ph.D. Associate Professor of Materials Engineering
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Research Staff:	A.W. Blackwood Research Assistant
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The effects of mechanical and chemical variables on the stress corrosion cracking susceptibility of copper-aluminum and copper-zinc alloys have been studied. Ammoniacal solution with different concentrations of pre-dissolved copper were the test environments. Time to failure at constant stress decreases with increasing pre-concentration of cupric ions which can form ammine complexes. This is due to the suppression by diffusional limitations of copper dissolution from the test samples, augmenting the formation of an adherent oxide film. The latter allows

failure to occur in the presence of a tensile stress by a film rupture mechanism.

Stress, and not prior plastic strain, was found to be the significant variable determining time to failure for copper-aluminum alloys. This and other information suggests that chemical reactions in the environment and prior dislocation content are less important than the length of dislocation pileups under dynamic conditions in causing failure.

The variable of solution pH is of itself of no importance in the stress corrosion process. It is, rather, a convenient way of describing the complex interaction of copper, ammonia and various acid ions over a wide range of conditions.

Unalloyed copper was found to be immune to genuine stress corrosion, contrary to reports in the literature of cracking in ammoniacal solutions pre-concentrated with cupric ions. Failure under these conditions has been shown in the present work to be a stress-rupture process.

#### METALLIC DISSOLUTION

Senior Investigator:	N.D. Greene, Ph.D. Professor of Metallurgical Engineering
Research Staff:	V. Colangelo, M.S. Graduate Assistant

The application of multiple correlation analysis to electrochemical data permits the prediction of the corrosion rate of an alloy as a function of its chemical composition. Using this method, previous studies have shown that significant improvement in the corrosion behavior of low alloy steels can be obtained by careful control of minor element content. This work is being continued in an effort to develop new low-cost corrosion-resistant alloys. Similar studies on the high alloy steels are planned also.

POLYMERS

## POLYMER RESEARCH

The physical properties of glasslike, elastomeric, and crystalline polymers are being studied and related to morphological and molecular structure. For crystalline polymers, electron microscopy on thin sections has been used in conjunction with optical microscopy to resolve the morphological features of the cold drawing process in nylon 66. Additional studies of crystalline morphology include wide and low angle x-ray diffraction, transmission and replication electron microscopy, calorimetry, and differential thermal analysis. Analysis of single crystals of polyethylene by density and heat of fusion techniques has helped to elucidate the defect density of the fold surfaces. Spherulite structure studies on polyoxymethylene, polyethylene terephthalate, and polypropylene, after a variety of crystallization conditions, thermal treatments and mechanical deformations, are giving insight into the relationship between structure and properties for high molecular weight, linear polymers. Variations of morphology from that encountered in commercial polymers are also considered. For example, extended-not folded-chain polymer crystals are produced by high pressure crystallization of polyethylene.

Research on the glassy state of high polymers includes inhomogeneous deformation studies on plastic deformation and craze formation, and the fracture of viscoelastic materials. Experiments involving well defined stress field perturbations are used to evaluate the material stress required to initiate a craze. The role of dilatation in the ductile failure of glassy polymers is studied by combination of simple shear and compound stress studies. Fatigue failure of polymers is studied and a mechanistic description of the role which viscoplastic deformation plays in the fatigue process is emerging.

Theories of the glass transition phenomenon require a more detailed knowledge of the structure of the glassy state of high polymers than is presently available.

Such information is sought using structure sensitive properties such as specific heat, glass transition temperature, and cohesive energy density, the latter being obtained through polymer-solvent interaction studies at constant volume. Kinetic aspects of the glass transition are studied by heat capacity hysteresis measurements made at different heating rates. The effect of molecular orientation on the thermal conductivity anisotropy of glassy polymers is being studied using highly drawn and quenched samples of glasslike polymers (PMMA) of different molecular weights.

Molecular characterization of sequence distribution in linear copolymers of poly(vinyl acetate) and poly(vinyl alcohol) is being sought by light scattering techniques. Infrared and x-ray spectroscopy studies of the same copolymers are coupled with dielectric spectra to yield a complete description of the molecular modes of motion and relaxations in this polar-polar copolymer system. Cryogenic studies on this copolymer system are in progress by the solid-state physics group. Included are cryogenic thermal conductivity, specific heat, and nuclear magnetic resonance data.

Theoretical research topics include the glass transition theory of high polymers, the thermal conductivity of high polymers, and the kinetic theory of rubberlike elasticity with emphasis on large deformations and equilibrium states as characterized by minimum free energy.

MECHANICAL PROPERTIES OF POLYMERS

Senior Investigator:	S.S. Sternstein, Ph.D. Associate Professor of Chemical Engineering
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A. Polymer-Solvent Interactions

An apparatus has been constructed in which glasslike, elastomeric, or polycrystalline polymers can be subjected to various degrees of liquid absorption, while the polymer is constrained to constant volume. Thermodynamic interaction parameters between the polymer and liquid can be determined by measurement of the pressure generated by the constant volume polymer sample. The apparatus has been designed to give continuous absorption versus time and pressure versus time analog signals, which can be recorded. Since the liquid being absorbed is at one atmosphere pressure (nominal), the pressure generated by the liquid-polymer interaction is a direct function of the thermodynamic driving force causing such interaction.

The system has been checked using a glasslike polymer (PMMA) and an elastomer (natural rubber). For the glasslike polymer, the pressure versus time curve, for several liquids, has been recorded for intervals as long as five days. Due to the thickness of the sample (1/8 inch), equilibrium was not obtained.



Thinner samples and higher temperatures will be used so that equilibrium absorption and pressure can be determined in a reasonable time scale. For the rubber sample, pressures as high as 300 psig were generated in forty minutes, but equilibrium absorption and pressure were not achieved. Due to the high pressures generated by rubber-liquid interactions, the equipment will be modified to incorporate a higher pressure transducer.

Glasslike sample having various thermal histories will be used in this apparatus, which may prove to be useful in the characterization of the excess entropy (or structural disorder) of the glassy polymer.

#### B. Fatigue of Glasslike Polymers

Low frequency cyclical loading of glasslike polymers is being carried out on a specially constructed apparatus which allows independent adjustment of the mean (creep) load value, dynamic load amplitude and frequency. The dynamic load is sinusoidal, and can be varied in frequency up to ca. 10 cps. The sample is loaded in uniaxial tension. Attempts will be made to measure the growth rates of small artificial flaws (cracks) under the fatigue loading conditions. Samples containing very thin deposited films of gold, which form part of a bridge circuit will be used to follow the growth of the crack. Also, a macrophotographic technique is being employed to follow the crack front.

#### C. Inhomogeneous Deformation in Polymers

Well defined stress field perturbations have been used successfully to determine the stresses required to initiate crazes in PMMA. By measuring the patterns formed by the crazes in the vicinity of a circular hole, in particular the boundary between the crazed and non-crazed regions, and comparing the boundaries with the known stress field about a hole, the threshold stress required to form a visible craze has been determined. The results are shown in Figure 1 as a function

of temperature. Of particular importance, it should be noted that these results are identical to the stresses required to cold draw a sample of PMMA in uniaxial tension at slow strain rate. Thus, it has been established that the local stresses required to establish an inhomogeneous deformation such as a craze are the same as for macroscopic plastic deformation. These results are for the craze pattern established after ten minutes of load application, and experiments are continuing on the kinetic aspects of craze propagation.

In a related series of experiments, special jaws have been designed to measure simple shear behavior of glasslike polymers. The problem of sample yielding inside the jaws has been eliminated. Results on the yield stress of PMMA versus temperature, in simple shear, are in the range of 1200 psi (about 25% of the yield stress) higher than one-half of the tensile yield stress. It appears that the dilatation which accompanies uniaxial tension does play a significant role in determining yield stress. It should be noted that most investigators infer the shear yield stress to be one-half of the tensile yield stress, assuming the dilatation effect to be negligible. Experiments on samples loaded in simple shear with a tensile stress applied normal to the shear plane will be conducted next to further establish the role of dilatation in yielding. (Part C is supported by N.I.D.R.)

#### D. Other Studies

The development of a constitutive equation for elastomer networks using minimum free energy considerations is continuing. Dielectric studies of the relaxations in polyvinyl alcohol-acetate are completed and are being prepared for publication. R.B. Watkins completed his Ph.D. thesis on the dielectric study during this report period.

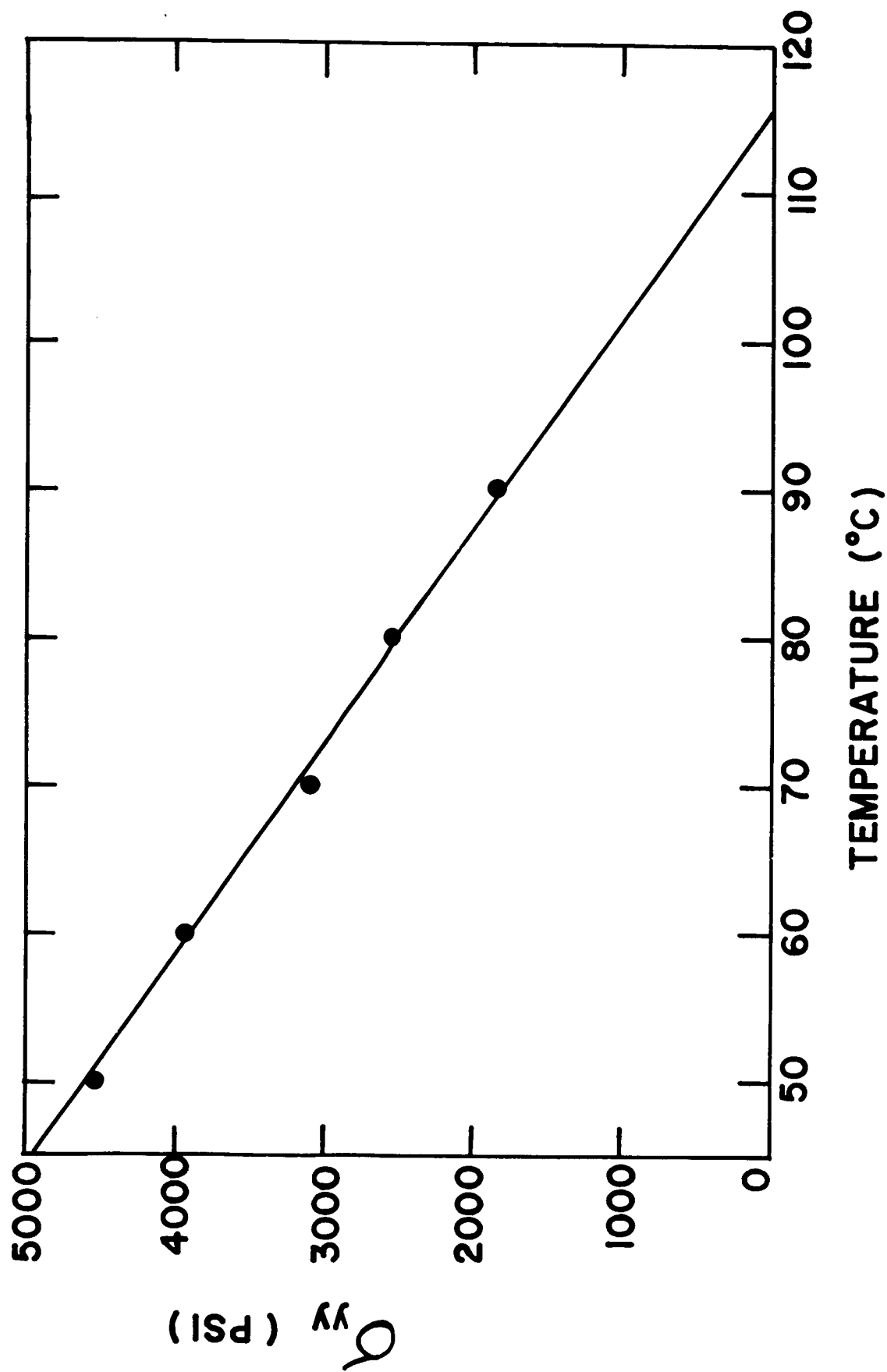


Figure 1 Normal Stress Required to Form a Craze in Polymethylmethacrylate as a Function of Temperature

THERMAL PROPERTIES OF POLYMERS

Senior Investigator: David Hansen, Ph.D.  
Associate Professor of Chemical  
Engineering

Research Staff: A. Bacon, B.Ch.E.  
Graduate Assistant  
R. Crystal, B.Ch.E.  
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Graduate Assistant

A. Thermal Conductivity

This investigation of the relationships between molecular geometry and heat conduction in polymers has yielded theoretical correlations of the effects of molecular weight and molecular orientation on the thermal conductivity of amorphous polymers. These correlations have been confirmed by specific experimental data. Experimental measurements are now being made on a series of oriented polymethylmethacrylates of different molecular weights to check the prediction from theoretical analysis that the effect of orientation on thermal conductivity will be molecular weight sensitive. Studies on oriented crystalline polymers are planned.

B. Morphology

Thin section electron microscopy on samples of nylon 66 and polyethylene terephthalate has identified two types of fibrillar spherulite structure. The first type has fibrils which are essentially long lamellar crystals in which the molecular axes lie tangential to spherulite radii. This type of fibril has been identified by numerous investigators from replication microscopy and indirect evidences. The second type of spherulite structure has fibrils which consist of stacks of small lamellar crystals with the molecular axes more nearly radial than tangential. Fibril structures similar to this have previously been noted in drawn

fibers, but have not been proposed to exist in undrawn polymers crystallized from the melt. Light microscopy observations and small angle x-ray scattering data support the interpretation of morphology from the thin section electron micrographs.

Further study of fibrillar structure is planned with particular emphasis on relating the morphology to crystallization conditions.

### C. Cold Drawing

In this study of morphological changes on cold drawing a nylon 66 composed of uniformly sized spherulites approximately 50 microns in diameter was examined before and after cold drawing by light and electron microscopy of thin sections and by low angle x-ray diffraction. Spherulites retained their identity through drawing, but the spherulites elongated less than the bulk specimen indicating that relative motion of spherulites must have occurred. The observation of dilations (0.3 microns long) at interspherulitic boundaries support this contention. The thin section electron micrographs indicated that the spherulites were composed of radiating lamellae approximately  $95 \text{ \AA}$  thick. After drawing the lamellae were preferentially oriented both parallel and perpendicular to the draw direction. Lamellae parallel to draw had thinned to approximately  $70 \text{ \AA}$  while lamellae perpendicular to the draw had apparently been compressed to a thickness of  $150 \text{ \AA}$ . Three low-angle x-ray diffraction patterns yielded quantitative agreement with the electron micrograph data. The pattern from the undrawn nylon was a diffuse ring corresponding to a  $95 \text{ \AA}$  spacing. On the drawn specimen, with the beam parallel to draw, a ring corresponding to the  $150 \text{ \AA}$  spacing was obtained while with the beam perpendicular to draw two arcs were recorded at spacing of  $70 \text{ \AA}$  and  $150 \text{ \AA}$ . The drawing was done at room temperature and proceeded by neck formation and propagation yielding a 4:1 draw ratio. It is planned to continue this work on specimens of various pre-draw structures subjected to different extensions, including draw ratios much larger than 4:1.

The studies of mechanical property changes on cold drawing, particularly the effects of repeated drawing and annealing, are continuing. (These studies of cold drawing are supported by the Army Research Office-Durham).

Since the last report period the following students have submitted theses and completed degree requirements: Walter H. Breyer, D.Eng.Sci., Richard G. Crystal, Ph.D., and Nancy C. Watkins, Ph.D.

#### POLYMER CHARACTERIZATION

Senior Investigators:	F.W. Billmeyer, Jr., Ph.D. Professor of Analytical Chemistry N.R. McFarlane, Ph.D. Assistant Professor of Organic Chemistry
Research Staff:	B. DiBona Undergraduate Assistant A. Eckard, B.Sc. Graduate Assistant P. Ghosh, Ph.D. Research Assistant S.Y. Hobbs, B.Sc. Graduate Assistant P.M. Holleran, B.Sc., M.Sc. (Esso Education Foundation Fellow) Graduate Assistant I. Katz, B.Sc. Graduate Assistant R.N. Kelley, B.Ch.E., M.Sc. Graduate Assistant P.J. Livesey, Ph.D. Supervisor, Polymer Characterization Laboratory T. Styk Undergraduate Assistant

#### A. Polymerization with the Sodium Sulfinyl Anionic Initiator

The production of the dimethyl sulfinyl ion by the reaction of dimethyl sulfoxide with potassium t-butoxide was studied. This species was used to initiate the anionic polymerization of methyl methacrylate. The molecular weight and molecular-weight distribution of the resulting polymers was studied by membrane osmometry, viscometry and gel permeation chromatography.

This project has terminated and a paper is in preparation.

#### B. Polymer Characterization

The initiation of vinyl polymerization by small (catalytic) amounts of sulfur dioxide is being studied with respect to kinetics and mechanism. Typical vinyl and diene monomers, such as methyl acrylate and methyl methacrylate, are studied. Despite the fact that a peroxide is required, possibly in the role of a co-catalyst, the ionic nature of the polymerization is demonstrated by the ineffectiveness of the usual free radical inhibitors such as hydroquinone. The reaction proceeds well at ambient or slightly elevated temperature, in contrast to most ionic polymerizations.

This work will be described in a paper, "Vinyl Polymerization Activated by Low Concentrations of Sulfur Dioxide," by P. Ghosh and F.W. Billmeyer, Jr., to be presented at the spring, 1968, national meeting of the American Chemical Society.

Other research under this project includes studies of the ultraviolet-light activated degradation of diene polymers.

#### C. Polymer Support

The electronics of the angular-dependence light-scattering photometer have been rebuilt with a significant improvement in signal-to-noise ratio. The instrument is now fully operational and in use in other projects described in this report.

A solvent-gradient elution column has been designed and is under construction for the small-scale preparative fractionation of polymers. A differential refractometer will be used to detect and monitor the effluent from the column.

As a byproduct of this work, a simple elution experiment, suitable for undergraduate laboratory use, has been devised to demonstrate the principles of separation by partition. This project was supported in part by the National Science Foundation, and equipment was donated by Waters Associates, Inc.

#### D. Heats and Entropies of Fusion of Polyesters

Single crystals of selected samples of linear aliphatic polyesters are being prepared by crystallization from solution and from the melt. Measurements of degree of crystallinity (x-ray diffraction, density) and heat of fusion (differential scanning calorimeter) will be made. Entropy of fusion will be calculated from the heat of fusion and the melting temperature. Entropies of fusion, as a function of ester-group spacing, will be compared with estimates of the unperturbed dimensions of polymer chains of the same type, obtained from solution studies.

This project is supported by the National Science Foundation.

#### E. Rapid Membrane Osmometry Diffusing Samples

A high-speed automatic membrane osmometer was used to study the apparent number-average molecular weights of well-characterized samples of branched polyethylene. These samples have broad molecular-weight distributions including species known to diffuse through osmotic membranes. Previous studies<sup>\*</sup> showed that conventional membrane osmometers, equilibrating in ca. 15 hours, gave apparent molecular weights two to three times higher than the true values, obtained with good agreement from the results of cryoscopy, ebulliometry, and vapor-phase osmometry. The present work shows conclusively that reducing the equilibration time (by two orders of magnitude) does not alone lead to correct results for these samples, although the apparent molecular weights were, as expected brought closer to the true values. Some experiments with different types of membranes were included.

This project has terminated and a paper is in preparation.

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<sup>\*</sup> F.W. Billmeyer, Jr., and V. Kokle, Journal of American Chemical Society, 86, 3544 (1964).

#### F. Sequence Distribution in Copolymers

Light scattering measurement in a variety of solvents will be used to study the sequence distribution in copolymers of vinyl acetate and vinyl alcohol, obtained



from the hydrolysis and, in some cases, partial reacetylation of poly(vinyl acetate).

#### G. Gel Permeation Chromatography

The fundamentals of the separation process of gel permeation chromatography are being studied. The principal effort is directed towards characterising the behavior of the separation columns by the application of the principles of gas chromatographic separation (particularly Van Deemter's equation) and of fluid flow in packed beds.

Preliminary results have been describe in two papers; "Application of Van Deemter's Equation to Gel Permeation Chromatography," by R.N. Kelley and F.W. Billmeyer, Jr., presented at the Fourth International Seminar on Gel Permeation Chromatography, May, 1967, and submitted to Separation Science, and "Evaluating Dispersion in Gel Permeation Chromatography," by R.N. Kelley and F.W. Billmeyer, Jr., presented at the fall 1967 national meeting of the American Chemical Society.

This project is supported by the Dow Chemical Company, Texas Division, and by the Water Associates, Inc.

#### H. Unperturbed Dimensions of Polymer Chains

Preliminary to a study of the unperturbed dimensions of linear aliphatic polyesters as a function of ester-group spacing, an effort has been made to confirm earlier work\* on the molecular weights and molecular-weight distributions of previously prepared polyesters of the 2,6; 2,8; 2,10; 4,6; and 6,6 types. This project will terminate in 1967 with the study of representative samples of each polyester type by light scattering and by gel permeation chromatography, and with synthesis studies designed to facilitate further sample preparation.

This work was supported by the National Science Foundation.

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\* E.A. Savaglia and F.W. Billmeyer, Jr., Official Digest, 36, 221 (1964); E.A. Savaglia, W.A. Mosher and F.W. Billmeyer, Jr., Ibid, 37, 229 (1965; P.S. Chang, E.A. Sanaglia and F.W. Billmeyer, Jr., Ibid, 37, 235 (1965)

IRREVERSIBLE THERMODYNAMICS OF THE SOLID STATE OF LINEAR HIGH POLYMERS

Senior Investigator:

B. Wunderlich, Ph.D.  
Professor of Chemistry

Research Staff:

F. Hamada, Ph.D.  
Postdoctoral Research Assistant  
S. Wolpert  
Graduate AssistantA. Time Dependent Specific Heats in the Glass Transition Region

The simplest description of a glass is offered by the hole theory of Eyring. One assumes that the melt contains an equilibrium number of holes characterised by uniform size and energy. At the glass transition temperature molecular motion becomes so slow that the hole-equilibrium freezes-in. A simple kinetic expression has been developed which allows the description of the hysteresis of heat capacity measured at different heating rates for samples of different thermal history. The sample analysed in the report period is poly(methyl methacrylate) which shows a smaller activation energy than the previously measured polystyrene despite almost identical glass transition temperatures. Further samples to be investigated include glucose, selenium and boron trioxide.

B. Density and Heat of Fusion of Folded Chain Polyethylene Crystals

The density of metastable folded chain single crystals of polyethylene has been a subject of intense scientific debate ever since our first measurements. The present research is completed and solved this problem. It was found that the method of measurement needed refinement. The small lamellae have such a large surface area that on drying to a mat after filtration it is impossible to wet the surface again completely for density measurement by immersion. A too low density results from the retained air. Crystals with irregular surfaces show the biggest effect. Only if the wet crystals are transferred into the immersion liquid is a true density measurable. Second order difficulties include preferential liquid absorption and surface oxidation.

The final densities obtained show a density approaching this of an x-ray perfect crystal at molecular weights below 10,000, and at high crystallization temperatures. Higher molecular weights, low crystallization temperatures and also broad molecular weight distributions lower the molecular weight drastically. Heats of fusion were also measured and indicate a 5 cal defect per square centimeter of surface of perfect crystals and an increasing amount for poorly crystallized samples. Indications are that the defect material is located at the surface of the crystal.

### C. Other Research

Other research of the senior investigator was supported by the National Science Foundation and the Office of Naval Research. The following research projects have been completed: a) Crystallization, Polymerization, and Melting of Polyoxymethylene and Selenium, b) Crystallization, Polymerization and Melting of Polycaprolactam, and c) Surface Morphology of Extended Chain Polyethylene. Continuing research is conducted on the production of extended chain polymer crystals by annealing, polymerization, and high pressure crystallization. A digital calorimeter is in the design stage. An extensive review of the heat capacities of polymers analysed on the basis of their vibrational frequency spectra is being prepared. A laboratory for characterization of the solid state of crystalline and amorphous polymers is maintained. Future research problems will involve the conformational analysis of superheating of polymer crystals on fast melting and the organic chemical and biological chemical aspects of simultaneous polymerization and crystallization. Support for the latter is sought.

### THE RELATION OF MOLECULAR STRUCTURE AND INTERMOLECULAR ACTION IN FLOW OF POLYMERS AND POLYMER DISPERSIONS AS A FUNCTION OF TEMPERATURE AND SHEAR RATE

Senior Investigator:

W.H. Bauer, Ph.D.  
Professor of Physical Chemistry

Research Staff:

T. Mass  
Graduate Assistant

The objective of the research has been to relate the flow properties of liquid polymers related to polybutadienes with the molecular structure and other properties of the polymers.

Apparatus and techniques have been developed for studying the flow properties of solutions of polybutadienes in appropriate solvents with the expectation that the flow properties will be related to the molecular structure.

SOLID STATE PHYSICS

## SOLID STATE PHYSICS

The tremendous progress that has come about in recent times in the technological uses of a multitude of materials both new and old has resulted from the combined efforts of many groups of scientists trained in diverse disciplines but with large areas of common overlap. Just because of this overlap there is a difficulty in characterizing distinctly the domain of any one such group as the solid state physicists.

Traditionally the solid state physicists have been concerned with ions, electrons, and radiation - with electron band structure, lattice dynamics and cooperative phenomena. There is a secondary interest in defects and only minimal concern with structure and microstructure in the metallurgical sense. Simple substances, pure materials and, if possible, single crystals are desirable for specimens but the tasks of their preparation and characterization are relegated to other specialists if available. Such simple systems are preferable because there is a better chance to correlate their behavior with idealized, mathematically tractable models which have always characterized the physicist's approach to theory. Solid state physicists frequently employ a considerable number of rather recently devised experimental techniques, often coupled to some microscopic resonance phenomenon and capable of high precision.

The principal experimental techniques featured by the solid state group in the Materials Research Center are magnetic resonance (both nuclear and electronic), ultrasonic propagation, x-ray diffraction, and thermal measurements in a liquid helium temperature range and below. There is an appreciable interplay between all of these.

The nuclear magnetic resonance has been very successful in exploring the mechanism of permanent polarization in ferroelectrics, particularly Rochelle Salt. In conjunction with radiation damage via  $\gamma$ -ray irradiation the nuclear magnetic

resonance has been applied to the study of defects in many salts. In the alkali halides the effect of stress induced field gradients has been explored and anti-shielding co-efficients have been calculated. The electron paramagnetic resonance technique has been employed in amorphous structures (glasses and amorphous selenium), in thin magnetic films (Fe-Ni and Fe-Co alloys), and in alkali halides where indirect evidence is being sought for the presence of interstitial complexes.

Most of the ultrasonic work has been carried on at low temperatures with the primary objective to use the thermal variation of attenuation in superconductors to determine the BCS gaps. A fruitful offshoot of this effort was the discovery and exploration of an amplitude dependent contribution to the attenuation. More recently evidence has been put forward for a difference in electron mean free path between normal and superconducting states. The ultrasonic attenuation is also amazingly sensitive to the presence of defects which, on becoming mobile at somewhat higher temperature can pin dislocations. This technique applied to lead irradiated with  $\gamma$ -rays at liquid nitrogen, has revealed a wealth of interesting effects that suggest specific models for lattice defect trapping. Ultrasonics has also been used at room temperature where the emphasis has been on elastic constant determination through velocity measurement. Ultrasonic beam-mixing has been demonstrated and the results used to give information on third order elastic constants. Ultrasonic measurements at high pressure (up to 50 kilobars) have been used to examine geologic materials and also pure substances. It has also been found in these laboratories that bone could be made to transmit ultrasonics under high pressure.

The intensity of x-ray diffraction peaks diminish with increasing temperature because the greater amplitude of the atomic vibrations tends to reduce the effectiveness of the Bragg scattering. The x-ray project in the Materials Research Center has concentrated on quantitative studies of this effect to gain another handle on elastic properties. So far zinc and several ferromagnetic alloys have been studied by this technique. The results supplement and to a large extent

confirm the conventional measurements of Debye temperature and elastic constants.

The low temperature facilities, which include one gear capable of going to  $0.4^{\circ}\text{K}$ , have clearly played a role in both the resonance and the ultrasonic work. In addition the  $\text{He}^3$  cryostat is being used to explore the thermal properties of polymers with some interesting and unexpected results. Apparently this is a nearly unexplored field and one rich in challenges for both experiment and theory.

There are many ways in which the research of the solid state group interacts strongly with the rest of the research in the Materials Research Center, of which these low temperature polymer studies are only the most recent example. (There are four strong polymer groups working in the NASA building). Other examples currently in progress are nuclear magnetic resonance studies of Al-Ag alloys with the group studying disperse hardening, the electron paramagnetic resonance work on amorphous materials with the ceramics program, and the thin film studies which hold interest in the area of memory application. As in other laboratories dedicated to materials research, the role of the solid state program is an essential and unifying one.



ULTRASONIC RESEARCH

Senior Investigator: H.B. Huntington, Ph.D.  
Professor of Physics

Research Staff: Russell W. Dunham, M.S.  
Graduate Assistant

Facility with the ultrasonic beam-mixing experiment has progressed to the point where the experiments can realize quickly and confidently almost any predicted situation for mixing two beams to give a third in the fused quartz specimen. Considerable progress has also been made in using the efficiency of such made conversion to give quantitative information on the third order elastic constants. Reproducible and reliable measurements are obtainable from the ratios of the conversion efficiencies for two situations (L T+T) where transmitter and receiver crystals for the transverse modes can interchange roles and where "straight-through" measurements can be used for receiver calibration. In this way compensation for faulty crystal bonding can be established and measurement reliability greatly increased. Additional quartz transducers have been purchased to make available transverse waves with frequencies from 5 to 25 Mcs. (The longitudinal sum frequency has been standardized at 30 Mc.) In this way relative conversion efficiency can be determined over a wide range for the ratio of the transverse waves frequencies. Good agreement is obtained with similar curves calculated from Bogardus' measurements of the third order elastic constants of fused quartz.

The beam mixing work also has didactic value as an experiment that illustrates 3-phonon collisions, absorption and induced emission. Huntington and Dunham have prepared a short TV tape from this point of view for classroom presentation.

The beam mixing in single crystal geometry has not previously been reported in the literature. A 4" diameter crystal cylinder of rocksalt has been purchased for a first attempt. In preparations for the experiments Dunham has explored analytically what appear to be the only possible mixing configurations involving solely pure modes.

The longitudinal beam directed down either the (100) or the (110) directions with the lower frequency transverse modes in the (100) plane and polarized perpendicular to it. By varying the frequency ratio for the transverse waves (and consequently their directions of propagation) it appears possible to develop two relations between the third order constants. Dunham is also plotting out the geometry for beam mixing involving impure modes but the analysis of the conversion efficiencies looks to be too involved to be worth attempting.

The ultrasonic data on anthracene is being reanalyzed.

#### NUCLEAR MAGNETIC RESONANCE IN SOLIDS

Senior Investigator:	P.A. Casabella, Ph.D. Associate Professor of Physics
Research Staff:	C.J. Miller, B.S. Graduate Assistant F.H. Huang, B.S. Graduate Assistant

The work on the relationship existing between electric field gradients and strain in alkali halides has continued. The studies of NaCl and NaBr are now completed, and work has begun on KCl, NaF and KBr. Each investigation requires three crystals of each compound, each at a different orientation. During the last six months we have carried out the preparatory work of crystal orientation and polishing.

In addition, two new projects have been successfully initiated. The first of these is a study of polymers at liquid helium temperatures by NMR. This work has been undertaken in conjunction with Dr. Salinger, and, as far as is known, it is the first such study attempted anywhere. To date the polymers studied include: nylon, polyethylene, polypropylene, poly methyl methacrylate (plexiglass), poly vinyl acetate polystyrene, and teflon. The most interesting results were obtained in poly methyl methacrylate and poly vinyl acetate in both of which was found that a methyl

group was rotating quite freely at  $4.2^{\circ}\text{K}$ . In the case of poly methyl methacrylate the temperature was lowered to  $1.3^{\circ}\text{K}$ , but the rotation continued, apparently unhindered. Both of these materials will be studied at still lower temperatures. in an attempt to observe the freezing out of this rotation. Another interesting result was obtained in polyethylene, where the only possible rotation in the molecule is a complicated crankshaft-like motion of a large section of the chain. This motion was observed to be present at  $77^{\circ}\text{K}$ , and it was possible to freeze it by going to  $4.2^{\circ}\text{K}$ .

The other new project, undertaken in conjunction with Dr. Ansell of Materials Engineering, was a study of the  $\text{Al}^{27}$  nuclear magnetic resonance in aluminum silver alloys. Thus far only the composition 95% aluminum and 5% silver has been examined.

This alloy must be prepared at a high temperature and when cooled to room temperature the silver precipitates out slowly and forms clusters. The results to date show no detectable change in the  $\text{Al}^{27}$  Knight shift as the silver precipitates. This means that the wave functions of the Al electrons at the Fermi level are not changed appreciably as the silver precipitates. This work will be continued by:

- 1) trying to increase the accuracy of the Knight shift measurement,
- 2) studying the shape of the resonance and
- 3) using other compositions.

#### ELECTRON SPIN RESONANCE

Senior Investigator:	A.C. Greene, Ph.D. Assistant Professor of Physics
Research Staff:	Vahakn Nalbandian, M.S. Graduate Assistant Thomas J. Santilli, B.S. Graduate Assistant Willard W. White, B.S. Fellow (N.S.F.)

Several projects of an interdisciplinary nature have been initiated and

will be continued. Magnetic properties of thin alloy films are currently being studied in conjunction with electron microscopy and other measurement techniques performed by members of the Materials Engineering Department. It is hoped that in studying the magnetic properties different structural phases of the films can be detected and determined. Studies are being conducted on such ferromagnetic alloy films as Fe-Ni and Fe-Co, as well as on paramagnetic films which include S-state ions in non-magnetic matrices. The films of primary interest are prepared by mechanical and chemical thinning, for comparison, initial experiments have been conducted on films prepared by evaporation.

Work on amorphous materials has been continued and expanded. Amorphous selenium, prepared under various heat quenching treatments, is currently being studied by electron spin resonance in order to determine molecular chain length and chain end interactions. These measurements are being correlated with electrical conductivity characteristics determined by members of the Materials Engineering Department. Further work on more standard polymeric materials is being initiated to study chain-end interactions. In these materials paramagnetism at chain ends can be induced by application of external stress. This work is also of interest to various groups in the Chemistry, Chemical Engineering, and Physics Departments.

Work is also continuing on the identification of the high temperature (near  $300^{\circ}\text{K}$ ) state of interstitial systems formed in irradiated crystals of the alkali-halide series. Attempts are underway to dissociate neutral diamagnetic molecular groups by thermal pulsing into atomic interstitialcy units which are paramagnetic and stable below  $77^{\circ}\text{K}$ . At high temperatures the presence of neutral molecular units can be monitored via nuclear magnetic resonance measurements. Also included in these studies is an extensive correlation with optical measurements.

X-RAY SCATTERING

Senior Investigator:	J.L. Katz, Ph.D. Professor of Physics
Research Staff:	S. Raman, Ph.D. Associate Professor of Physics J. Feldman, Ph.D. Research Assistant E.F. Skelton, Ph.D. Research Assistant G. Krycuk Research Assistant R. Ramachandran, B.E.E. Graduate Assistant

The basic research presently being continued under the support of the National Institute of Dental Research and the U.S. Army Research Office (Durham) at the Rensselaer Interdisciplinary Materials Research Center falls into three complementary areas: lattice dynamical force model calculations, thermal motion studies, and high pressure investigations.

In an attempt to improve on the previous calculation of the thermal diffuse scattering (T.D.S.) contribution to the measured, integrated x-ray intensity scattered from a zinc single crystal, the modified axially symmetric force model of DeWames et al. is being employed. This calculation involves summing the contribution to the measured T.D.S. from each lattice wave having a wave vector which terminates within the region carved out of reciprocal space during the intensity scan.

The General Electric XRD-5 diffractometer is presently being equipped with a LiF doubly-bent monochromator and full circle  $\omega$ -motion. Once operational, it is hoped that these refinements will allow measurement of the T.D.S. at the forbidden reflections in zinc, and thus afford an experimental check on the aforementioned calculations.

Additional low temperature measurements of the mean square atomic displacement differences parallel to the hexagonal axis, and lying in the basal plane,

of zinc have recently been completed down to  $4.8^{\circ}\text{K}$ . These additional data, in conjunction with earlier data in the higher thermal range ( $30^{\circ} \leq T < 600^{\circ}$ ), permit a self-consistent evaluation of the absolute values of the two principal mean square displacements at room temperature. The mean square displacements have been employed to evaluate the x-ray Debye temperature over the thermal range involved and comparison of these results with recent model calculation, as well as with other Debye temperatures for zinc, has proven rather informative. These results have been presented at the Summer Meeting of the American Crystallographic Association and are being prepared for publication.

The high pressure investigations are directed primarily at determining the elastic behavior of biostructural materials, i.e., bones and teeth and prosthetic and restorative materials such as dental amalgam in a high pressure environment. High pressure ultrasonic measurements of the elastic constants of a wide compositional range of dental amalgams were presented at the Dental Materials Session of the 1967 A.I.M.E. meeting. Results for deorganified bone material and various calcium phosphate, i.e., apatites, were reported at the March 1967 meeting of the International Association for Dental Research. The aforementioned results are being currently prepared for publication along with elastic constant measurements on bovine dentin and enamel performed this summer.

#### ULTRASONIC PULSE INTERFEROMETRY

Senior Investigator:

S. Katz, Ph.D.  
Professor of Geophysics

Research Staff:

R.S. Gilmore, M.S.  
Research Assistant  
H.B. Reed, B.S.  
Graduate Assistant  
R.N. Schock, Ph.D.  
Research Assistant

The high-pressure optical study of AgI, mentioned in previous progress

reports and in press in the Journal of Physics and Chemistry of Solids, has been extended by measurements of electrical conductivity to nearly 100 kbar. Each of the polymorphic transitions were detected. The conductivity increases anomalously with pressure initially, in agreement with published results and then decreases above the IV-III transition (orth-fcc). A manuscript is in preparation on this work.

Experimental work performed intermittently during the past two years on the pressure-dependence of the infrared absorption of  $\text{CaCO}_3$  (calcite) has been completed and the resulting manuscript submitted for publication. The absorption was measured to over 20 kb in a Bridgman diamond-anvil squeezer. The appearance of new bands and the change in band width and depth are consistent with a transition from calcite to aragonite structure near 4 kb.

#### ULTRA-LOW TEMPERATURE SOLID STATE PHYSICS RESEARCH

Senior Investigator:	G.L. Salinger, Ph.D. Assistant Professor of Physics
Research Staff:	Y.C. Chiang, M.S. Graduate Assistant C.L. Choy, B.S. Graduate Assistant

The thermal conductivity of several amorphous polymers has been measured between 0.4 and 4.2°K. The results on polymethyl methacrylates of different molecular weight, polystyrene, and polyvinyl acetate are qualitatively similar. The conductivity is independent of temperature near 4°K and decreases with an ever increasing power of temperature as the temperature is decreased. Thus the linear dependence of the thermal conductivity predicted by theory when the wavelength is long compared to microscopic disorder is not found. The thermal conductivity increased about 8% when the molecular weight was increased by a factor of ten. The affects of chain ends will also be investigated by orienting samples by stretching them about 400%.

The thermal diffusivity was measured in the same polymers down to 1.5°K where the time constants became too short. From these measurements, the specific heat can be extracted. In all cases the specific heat was proportional to  $T^3$ , but larger than predicted by elastic measurements. Apparatus has been designed to be able to make classical specific heat measurements to lower temperatures. This will be useful in interpreting the thermal conductivity data.

Similar measurements have been made as a function of crystallinity in polyethylene. The thermal conductivity can be described by  $K = AT^a$  over the entire range of temperature where  $A$  and  $a$  depend on the crystallinity.  $a$  increases from 1.6 to 2.2 as the crystallinity increases from 70 - 92%.  $A$  also increases with crystallinity. The specific heat decreases slightly as the crystallinity increases as previously observed above 2°K.

Measurements of the ultrasonic velocity in polymers down to liquid nitrogen temperatures are in progress to help elucidate the observed. Acoustic bonding problems are being overcome.

Together with Dr. P.A. Casabella, we are making preliminary nuclear magnetic resonance measurements on a number of polymers at room temperature, 77°K and 4.2°K. To our knowledge, these are the first liquid helium temperature, measurements. The methyl groups at the end of the pendant groups in polymethyl methacrylate and polyvinyl acetate seem to be still rotating at 1.30°K. This work has a bearing on the understanding of the specific heat and will be vigorously pursued.

The sound velocity and the nuclear magnetic resonance experiments are being performed by personnel not sponsored by NASA but on our equipment. We also acknowledge the help and interest shown by the other polymer groups in the Interdisciplinary Materials Research Center laboratory.



LOW TEMPERATURE PHYSICS

Senior Investigators:	R.W. Shaw, Ph.D. Associate Professor of Physics
	G.L. Salinger, Ph.D. Assistant Professor of Physics
Research Staff:	Br. A. David Detje, B.S. Graduate Assistant W.A. Fate, B.S. Graduate Assistant H.J. Willard, M.S. Graduate Assistant D.S. Woo, B.S. Graduate Assistant

The ultrasonic attenuation studies in superconducting lead, mercury and thallium have been completed and the data have been analyzed. Three Ph.D. thesis have been accepted for this work, and one letter has been published. Other articles are being prepared for publication. The main new experimental results of the last six months have been the determination of superconducting energy gaps in thallium from the superconducting to normal acoustic attenuation ratios. The energy gaps determined in three directions from the data obtained below  $0.8^{\circ}\text{K}$  (obtained on the cryostat built under this NASA contract) agree very well with gaps obtained by other means.

The study of the migration of point defects in cobalt-60  $\gamma$ -irradiated lead is yielding interesting results. Activation energies and diffusion constants have been measured for various processes. Interpretive experiments are being done to determine a model for the annealing observed. This work will culminate in a thesis during the next six months.

The study of ultrasonic attenuation in mercury yielded (as a by-product) acoustic velocities quite different from those previously reported. Appropriate single crystals of mercury are being grown and oriented. The acoustic velocities are being measured interferometrically.

DIFFUSION FACILITY

Senior Investigator: H.M. Gilder, Ph.D.  
Assistant Professor of Physics

Research Staff: G. Wallmark, B.S.  
Graduate Assistant

The high terminal solubility of gallium in aluminum ( $\sim 5$  at. %) makes Al-Ga a promising alloy in which to study the effect of solute concentration on solute and solvent tracer diffusion coefficients in a "valence three" metal.

To date the research effort has primarily centered on finding a way of counting  $\text{Al}^{26}$  at extremely low specific activity such that one obtains a reasonably high gross count rate and as large a ratio of "gross" to "background" count rate as possible. Counting the annihilation gammas in coincidence has so far offered the most promising means of counting  $\text{Al}^{26}$ .

A suitable diffusion furnace has been built with the help of graduate assistant Gerald Wallmark, and air alignable chuck, to be used in the lathe sectioning, is near completion.

TECHNICAL PAPERS SUBMITTED FOR PUBLICATION

Members of Faculty Committee on Interdisciplinary Materials Research

FINANCIAL INFORMATION

TECHNICAL PAPERS SUBMITTED FOR PUBLICATION

Katz, S., Schock, R.N.

"High Pressure Study of AgI: Diffusion in a Pressure Gradient"  
To be published in Journal of Physics and Chemistry of Solids

Katz, S., Schock, R.N.

"Pressure Dependence of the Infrared Absorption of Calcite"  
Submitted to American Mineralogist

Shaw, R.W., Fate, W.A.

"Amplitude-Independent Ultrasonic Attenuation in Superconducting Lead"  
Published in Physics Review Letters 19, 230, 1967

Bauer, W.H., Boyce, R.J., Collins, E.A.

"Flow Behavior of Low Molecular Weight Polybutadiene, Carboxyl-Polybutadiene,  
and Butadiene-Acrylonitrile Copolymers"  
Published in Transactions of the Society of Rheology, 10:2, 545-570 (1966)

Greene, N.D., Cleary, H.J.

"Corrosion Properties of Iron and Steel"  
Submitted to Journal of Corrosion Science

Katz, J.L., Wilson, R.H.

"Temperature Dependence of the X-Ray Debye Temperature in a 33% Nickel in  
Iron Alloy"  
Submitted to Journal of Acta Crystallographica

Wunderlich, B., Hamada, F., Hayashi, S., Nakajima, A., Sumida, T.

"Density and Heat of Fusion of Folded Chain Polyethylene Crystals"  
To be submitted to Journal of Physical Chemistry

Hansen, D., Crystal, R.G.

"Morphology of Cold Drawn Nylon-66"  
Submitted to Journal of Polymer Science

MEMBERS OF FACULTY COMMITTEE ON INTERDISCIPLINARY  
MATERIALS RESEARCH

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F.V. Lenel	Professor of Metallurgical Engineering and Chairman of the Department of Materials
S.S. Sternstein	Associate Professor of Chemical Engineering
J.M. LoGiudice	Administrative Director of the Interdisciplinary Materials Research Center